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# Catalytic Conversion of Alcohols: Role of Sodium in Altering the Alkene Products Obtained with Alumina Catalysts

Investigators frequently use alkali poisons in an effort to eliminate secondary reactions and, thus, to obtain the primary product distribution when using alumina as a catalyst or support (*1, 2*). This poisoning of alumina by alkali ions has been noted by many authors. Pines and Haag (*3*) found that alkali was a severe poison for the dehydration of 1-butanol with alumina. Also, Ross and Bennett (*4*) determined the influence of metal ions on alumina-catalyzed dehydration of ethanol and observed that alkali was a poison whose effect was consistently more pronounced at higher alcohol pressures. Maatman and Vande Griend (*5*) found that impregnation with LiCl, NaCl, KCl, or $CaCl_2$ deactivated alumina for 1-butanol dehydration, although in some cases at low salt concentration a promotional effect was observed. Pscheidl and Witzmann (*6*), using 2-propanol and Li-doped alumina, and Pis'man and co-workers (*7, 8*), using 1-butanol and KOH-doped alumina, reported an initial increase, followed by a decrease, in activity as alkali concentration was increased.

Catalytic activity is difficult to accurately measure for a reaction such as alcohol dehydration where the alcohol reactant and a product, water, may be strongly absorbed. Selectivity may be used together with activity to provide a more accurate picture of the reaction mechanism.

The catalysts were prepared by impregnating Degussa aluminum oxide C with aqueous sodium nitrate using the incipient wetness technique. The impregnated alumina was dried at 120°C and then calcined at 500°C in air. The alcohol conversions were carried out in a plug flow reactor. A mixture of 2-butanol (25 mole%) and 2-octanol was converted after activating the catalyst at 500°C in air for 4 h. Conversions were effected at atmospheric pressure without added carrier gas. Liquid products were collected at intervals and were analyzed for total conversion by GC using a Carbowax 20M column. Butene gas samples were collected in a gas syringe and were analyzed using a $\beta,\beta'$-oxydipropinonitrile column.

A pseudo-rate constant was calculated from the data for the conversion of 2-octanol. Plots of conversion of 2-octanol vs $\text{flow}^{-1}$ (space time) were reasonably linear for the higher flow rates (lower conversion) as is required for a zero-order reaction. Alcohol dehydration, at higher alcohol pressures, has been shown to be a zero-order reaction (*9–11*). The activity and selectivity of alumina for alcohol dehydration may depend on pretreatment (*12*). This was especially true for the activity of Degussa alumina and the rate value shown in Fig. 1 is an average of several runs using different portions of a single alumina preparation. Even so, it is apparent that sodium decreases the amount of alcohol dehydration as reported by earlier investigators.

The products from the alumina-catalyzed dehydration of 2-butanol, at up to one atmospheric alcohol pressure, differ from those obtained when 2-butanol is converted in the presence of 2-octanol (*13*) or nitrogen base (*14*). At temperatures near 200°C it appears that the relative pressure of 2-butanol is too low to inhibit alkene isomerizations by secondary reactions. For example, at 200°C the relative pressure for 2-butanol is approximately 0.05 while that of 2-octanol is 0.5 or greater. Thus, this secondary isom-

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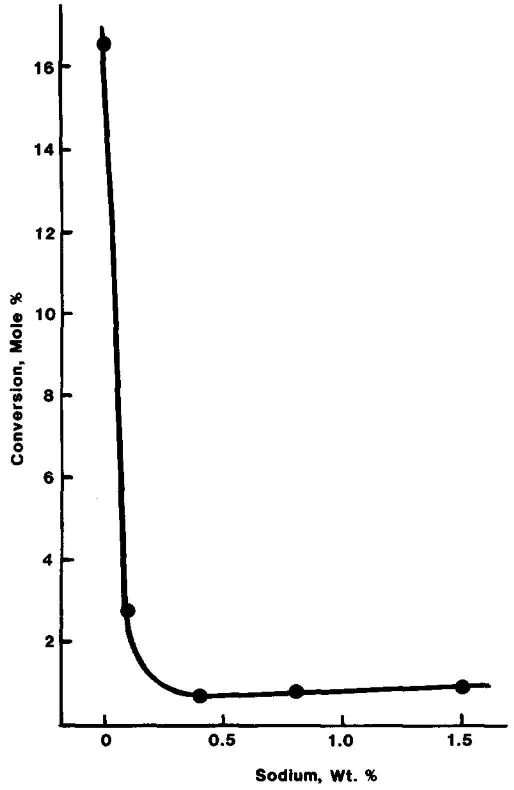

FIG. 1. The pseudo-rate constant for the conversion of 2-butanol/2-octanol mixture with alumina and sodium-poisoned alumina.

erization may be inhibited by 2-octanol better than by 2-butanol. For this reason, a mixture of 2-butanol and 2-octanol was used in this study.

The amount of 1-butene does not change appreciably at longer reaction times from that obtained for the initial sample (Fig. 2). Even where it does show a small change, as in the initial samples with pure alumina, the *trans*-2-butene content remains essentially constant while the amount of 1-butene increases with a concurrent decrease in *cis*-2-butene. Thus it appears that the initial alkene selectivity changes are the result of a small amount of secondary isomerization of the 1-butene to *cis*-2-butene; a selectivity that is well documented for alumina (*2*).

The alkene compositions for alumina and alkali-poisoned alumina are shown in Fig. 3. The selectivity trend, with increasing alkali content, is obvious: the amount of 1-butene decreases more rapidly than the *cis*-2-butene and the amount of *trans*-2-butene increases. The alkene compositions shown in Fig. 2 were obtained for four different flow rates; no change in selectivity was

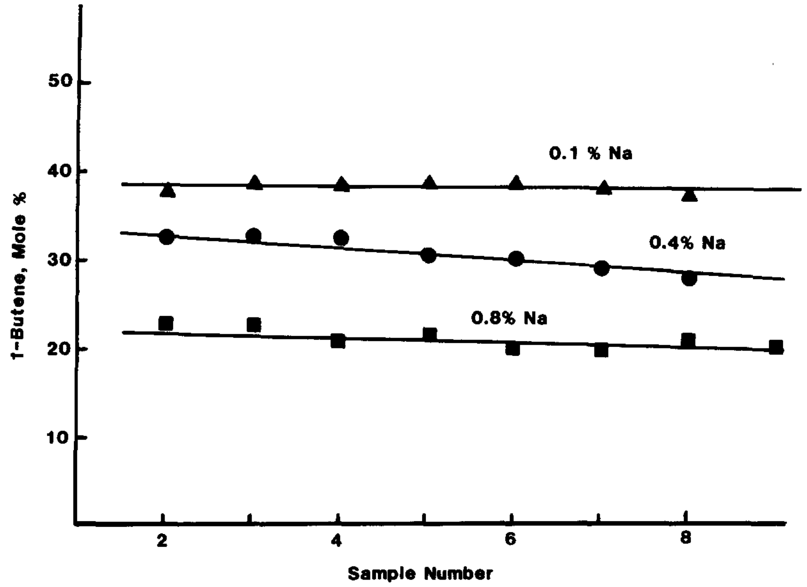

FIG. 2. Alkene distribution with time-on-stream from the dehydration of 2-butanol with alkali-poisoned catalysts.

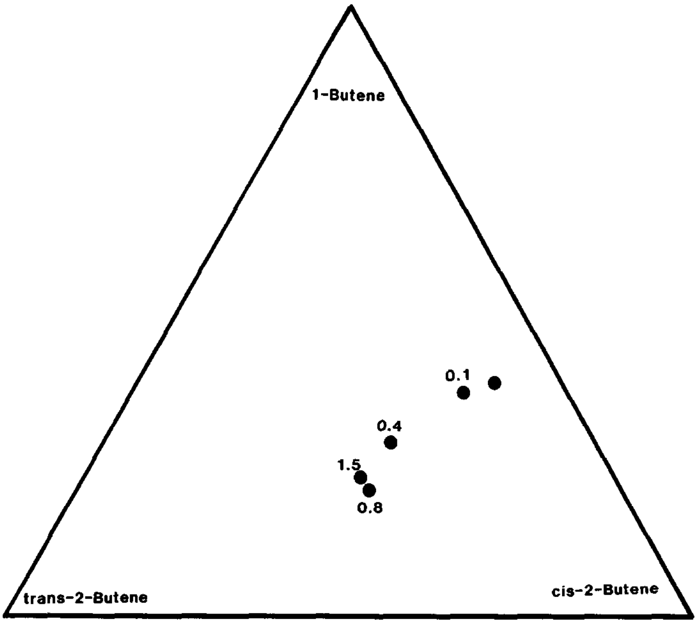

FIG. 3. The alkene distribution for the conversion of 2-butanol with alumina and alkali-poisoned alumina (the numbers refer to the sodium content).

noted for increasing space velocity (and decreasing conversion). Thus, the addition of alkali to alumina causes a drastic change in the initial alkene product distribution rather than by eliminating secondary reactions.

It is well established that the isomerization of 1-butene produces a high *cis/trans* ratio for the 2-butene products (*15*). The *cis*-2-butene appears to isomerize to *trans*-2-butene more rapidly than to 1-butene (*16*). Base-catalyzed isomerization is very selective where 1-butene isomerizes, using a supported NaOH catalyst, to predominately *cis*-2-butene and *cis*-2-butene to 1-butene (*17*). Also, high temperatures (400°C or more) are required for the base-catalyzed isomerizations. Thus, an isomerization catalyzed by strong base does not appear to be present in our studies. Some alumina-catalyzed alteration of the primary alkene products may be possible. However, both Dautzenberg and Knözinger (*18*) and Davis (*13*) obtained results with 2-butene that were consistent with the 1-butene, initially formed, isomerizing to *cis*-2-butene; this was not observed by workers using 2-octanol (*13*) or nitrogen bases as poisons (*14*). For alkali-poisoned alumina the amount of *cis*-2-butene is not greater than was obtained with pure alumina. Thus, it appears that the butenes are formed by a mechanism other than normally observed for secondary isomerization reactions.

The present results could occur if the alumina catalyst possessed two types of dehydration sites. One type of site, designated A, is much more active for dehydration than is the other type, designated B. The A sites selectivity form 1-butene and *cis*-2-butene in about equal amounts but only a small fraction of *trans*-2-butene; B sites form each of the three isomers in nearly equal amounts. The selectivity, and the low activity, of type B sites appear similar to those of α-alumina (*19*). We postulate that type A sites represent those coordinately unsaturated sites, similar to the Taylor concept of active sites (*20*), which are very active and impose steric requirements to produce selectivity in the alkene formation. Type B sites would be those low activity sites found on reasonably uniform, low curvature crystal faces, such as found on low surface area α-alumina.

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